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Preparation of Portland Cement Components by PVA Solution Polymerization

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Abstract

The four components of Portland cement: dicalcium silicate, C_2S (Ca_2SiO_4), tricalcium silicate, C_3S (Ca_3SiO_5), tricalcium aluminate, C_3A ($Ca_3Al_2O_6$), and tetracalcium aluminate iron oxide, C_4AF ($Ca_4Al_2Fe_3O_{10}$), were formed using a solution-polymerization route based on polyvinyl alcohol (PVA) as the polymer carrier. The powders were characterized using X-ray diffraction techniques, BET specific surface area, and scanning electron microscopy. This method produced relatively pure, synthetic cement components of sub-micron or nanometer crystallite dimensions, high specific surface area and extremely high reactivity at relatively low calcining temperatures. The PVA content and its degree of polymerization had a significant influence on the homogeneity of the final powders. Two types of degree of polymerization (D.P.) PVA were used. Lower crystallization temperatures and smaller particle size powders were obtained from the low D.P. type of PVA at optimum content.

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I. Introduction

Ceramic processing has been using chemical synthesis routes in more recent years.¹⁻¹⁰ Methods based on soft-solution processing provide powders with desired properties such as high purity and homogeneity.^{1,4,6} In particular, polymer-metal cation complexes are interesting because of their ability to produce well-characterized materials for various industrial purposes and practical uses. In recent years, a new technique has been developed in powder synthesis processing, viz. the use of a polyvinyl alcohol (PVA) as a polymeric carrier in a metal-mixed solution. By using the PVA process, ceramic powders are synthesized much more easily than in other chemical synthesis routes.²⁻⁶ The PVA ensures the homogenous distribution of the metal ions in its polymeric network structure and inhibits their segregation/precipitation from the solution.¹⁻⁵ One can visualize this process in terms of the polar groups of the polymer long chain wrapping themselves around the cations in the solution. Contact between cations is avoided, and this limits their growth and ability to precipitate prematurely. The PVA process also produces carbonaceous material that gives heat through its combustion, so that fine and single phase powders can be formed at a low external temperature.¹⁻⁵ Initially, Gulgun et al²⁻³ synthesized compounds such as calcium aluminate (CA) and yttrium aluminate garnet (YAG) phases using the PVA technique. Unlike the Pechini-resin process,^{7,11-14} which involves chelation and polymerization, the PVA process involves primarily steric entrapment of cations into the polymer network.³⁻⁵ The steric entrapment mechanism results in a pure, highly reactive, and homogenous powder at the molecular level.

Some of the Portland cement components have been made by other chemical synthesis routes. Kralj et al¹⁵ were able to produce C_2S at $950^\circ C$ but this required repeated firings of up to four times, with grinding in between each firing to complete the reaction. Roy et al⁸ also experimented with C_2S and C_3S to form the materials by a chemical process by nitrate salts and an aqueous sol of SiO_2 . They used both the spray-dry technique and gel preparation methods, and obtained BET specific surface area values of $12.94 \text{ m}^2/\text{g}$ for C_2S and $12.87 \text{ m}^2/\text{g}$ for C_3S .

In this study, the four components of Portland cement; dicalcium silicate (Ca_2SiO_4), tricalcium silicate (Ca_3SiO_5), tricalcium aluminate ($Ca_3Al_2O_6$), and tetracalcium aluminate iron oxide ($Ca_4Al_2Fe_3O_{10}$), were made by the PVA process. By using this method, it was possible to control chemical and physical characteristics, to synthesize at lower temperatures, to eliminate grinding-refiring steps mentioned above, and to produce a high powder yield.⁶ Optimum synthesis conditions, such as PVA content, degree of polymerization of the PVA, and calcination temperature, were determined for each component. The powders were characterized by microstructural examination (XRD, SEM)

and specific surface areas were measured by nitrogen gas adsorption BET. The powders prepared by this new application can make pure, synthetic, cement components of nano or sub-micron crystallite dimensions, high specific surface area, and extremely high reactivity at relatively low calcining temperatures, in comparison with conventional methods.¹⁶ It is then possible to explore the realm of advanced cementitious materials and its interdisciplinary interface with ceramic synthesis and processing. Once the hydraulicity of each component is determined as a function of the powder characteristics, it is possible to optimize various compositions for specific applications, such as enhanced setting speed, higher strength and other desirable characteristics.¹⁷⁻¹⁹

II. Experimental Procedure

(1) Powder Processing

The nitrate salts were in the form of cation sources with the exception of silica which was supplied as a colloidal silica product (Ludox SK, 25% silica sol, DuPont, Wilmington, DE). The chemical reagents and product manufacturers are listed in Table I. These cation sources were dissolved in stoichiometric proportions in de-ionized (DI) water. To improve the process of dissolving the Ludox SK, the pH of the solution was adjusted by addition of nitric acid. Once the cation sources were completely dissolved, the 5 wt% PVA (Air Products and Chemicals, Inc., Airvol Series, Allentown, PA) was dissolved in DI water and added. The degree of polymerization (D.P.) of the PVA was varied in these experiments. The high D.P. PVA was made from Airvol 540S, with a D.P. value of 1625 (monomers/polymer), and the low D.P. PVA was made with Airvol 205S with a D.P. of 428 (monomers/polymer). The high D.P. PVA had a molecular weight of 153,000 and the low D.P. PVA had a molecular weight of 40,000. The proportions of the PVA to cation sources in the solution were adjusted in such a way that there were 4, 8, or 12 times more positively charged valences from the cations than the negatively charged (OH)⁻ functional groups of the polymers. In the case of the 4:1 PVA content ratio in C₂S, the total positively charged valences were eight. Thus, two PVA monomers (one monomer has one (OH)⁻ functional group) were used per one mole of C₂S. Water was evaporated by continuous stirring during heating on a hot plate. The gel-type precursor was completely dried at 100°C after approximately 12 hours. The organic/inorganic precursors were then ground and kept in a dessicator because of their hydrophilic characteristics. Each of the ground precursors were calcined or crystallized at various temperatures in an air atmosphere in a box furnace. Each of the four components were calcined at a rate of 3°C/min. Crystallized C₃S and C₃A powders were attrition milled to examine the effects of milling on the surface

area. The powders were attrition milled at 240 rpms for 1 hour (Szegvari Attritor System Type B, Union Process, Akron, OH). Approximately 700 g of zirconia milling media (ball diameter: 5 mm) were mixed with 100 ml of methyl alcohol in a 600 ml jar.

(2) Characterization

(A) *X-ray Diffraction Analysis* : The crystallization behavior of each of the calcined powders was studied as a function of temperature and holding time at elevated temperatures, using a Rigaku spectrometer (Dmax automated powder diffractometer, Rigaku/USA, Danvers, MA) with CuK_α radiation (40 kV, 40 mA). All XRD data was obtained at room temperature, after the powder had been cooled. A scanning speed of 10 °/min with a sampling interval of 0.02° over a range of 10-70° for C_2S , C_3S , and C_3A was used. For C_4AF the range varied from 30-40°.

In C_3A , the relative volume ratios of C_3A and residual CaO phases were determined by integrating the X-ray peak areas of (440) of C_3A and (200) of CaO by the equation:

$$V_{\text{C}_3\text{A}} = [\text{I}(440)_{\text{C}_3\text{A}} / (\text{I}(200)_{\text{CaO}} + \text{I}(440)_{\text{C}_3\text{A}})] \times 100$$

in which, $V_{\text{C}_3\text{A}}$ is the volume fraction of C_3A , and $\text{I}(440)_{\text{C}_3\text{A}}$ and $\text{I}(200)_{\text{CaO}}$ are the 100 % peak intensities of C_3A and CaO , respectively.

(B) *Specific Surface Area Measurement* : The specific surface area of the crystallized powders and attrition milled powders were obtained by five-point BET analysis from nitrogen gas adsorption (Model ASAP 2400, Micromeritics, Norcross, GA). All samples for testing were kept in a dry oven to prevent hydration of the powders.

(C) *Microstructure Characterization* : The morphologies of calcined, crystallized, and/or attrition-milled powders were examined by scanning electron microscopy, SEM (Model Hitachi S530, Hitachi, Japan). For the SEM specimens, each powder was completely dried, attached to an aluminum stub, and gold sputter coated.

III. Results and Discussion

The optimum pH's for C_2S and C_3S to form transparent solutions and stoichiometric powders are listed in Table I. For each of the four components, the binder was completely burned out by 700°C. With respect to the characteristics of the dried precursors, both C_3A , and C_4AF resembled an aerogel formed by foaming during the stirring and solution drying process. The foam mainly resulted from elimination of NO_x gas from the aluminum nitrate source.

(1) *Crystallization Behavior*

Table II and III summarize the X-ray diffraction data acquired for each of the four powders, for high and low D.P. PVA, respectively. The effect of D.P. was particularly evident in the 700°C calcining range for C_2S and C_3S . In the high D.P. route, the amorphous phase was still present while with the low D.P. PVA, the calcined powders were crystallized. In the case of single phase C_3A (> 95 vol%), the powder prepared via low D.P. PVA crystallized at 1000°C/ 1 h. By comparison 1100°C/ 3 h conditions were necessary to crystallize relatively pure C_3A made by the high D.P. PVA. C_4AF showed no apparent changes in its crystalline behavior.

The effect of degree of polymerization of the PVA may be attributed to the following considerations. The low D.P. PVA had smaller polymer chain lengths than did the high D.P. PVA, so it could make the range of distances between cations in the solution shorter.⁴ This is especially important in the synthesis of C_3A and C_3S because the concentration of Ca^{2+} ions is much higher than of Al^{3+} or Si^{4+} ions. This can lead to unreacted CaO phase at even high temperatures. For the compound to be synthesized at low temperatures, the Ca^{2+} ions and Al^{3+} or Si^{4+} ions must be homogeneously dispersed within short range of each other. The chain length of the lower D.P. PVA was small enough for this mixing to occur in the steric entrapment mechanism. Furthermore, the higher amount of PVA (4:1 ratio) added to the solution aided in this mixing process. The low D.P. PVA distributed the metal ions homogeneously, so that after binder burnout, the network shrank enabling C_3A or C_3S to be formed more readily. The cations were sterically trapped within short range of each other and formed organic precursor complexes.^{3,4} Thus, it did not require as high a temperature to form the compound.

Figure 1 shows the effect of the PVA content on the crystallization of C_3A . The volume fraction of C_3A was determined by comparing the ratio of the integrated area of the 100% intensity peak for CaO with the 100% intensity peak for C_3A . In the low D.P. PVA process the volume fraction of C_3A increased with the increasing PVA. The best result was obtained with the low D.P. PVA in the 4:1 ratio. This implies that in the low D.P. PVA system, the higher content of PVA did not make a significant difference in the distance between cations, but rather it improved the homogeneity of the distribution of cations. In the high D.P. PVA system, the 8:1 ratio showed the highest volume fraction of C_3A . This may be attributed to the high D.P. PVA chain lengths being longer than the low D.P. PVA, so that in the 4:1 case the cations could not get close enough to one another to form a compound. The solution had a high viscosity with inhomogeneities caused by the entanglements of the long-chain PVA molecules in excess amount. Once this ratio was

changed to 8:1, the results improved dramatically because the metal ions could get close enough to one another to form C_3A . Because PVA is not an expensive chemical, it may be more economical overall to use more PVA in conjunction with the lower D.P. PVA, so as to achieve the best result possible, rather than calcining at 100°C higher and for 2 hours longer by using the high D.P. PVA. The 12:1 case is the most undesirable for both the low and high D.P. PVA because there simply was not a high enough PVA content to make a homogenous mixture. Agglomeration can also occur at the 12:1 PVA ratio, and hence the specific surface area was decreased.^{4,5}

(B) BET Specific Surface Area

Table IV summarizes the BET specific surface area of each powder at the optimum crystallization conditions which had the lowest crystallization temperature. Except in the case of C_3S , the surface area increased with the use of the low D.P. PVA. This may be attributed to lower crystallization and hence decreased sintering between particles. The higher the specific surface area, the faster the hydration, which decreases the setting time in cements.¹⁸ Attrition milling for 1 h can also dramatically increase the specific surface area, because of the breaking up of the pre-sintered, coarse powder agglomerates. By attrition milling, an extra step has been added to the formation of these high specific surface area powders, as well as an extra expense. However, after only one hour of milling, the surface area was increased by more than 50 times in the case of C_3S and by more than 4 times for C_3A . C_3S is known for its ability to hydrate rapidly, to be responsible for the initial set, and to provide early strength to portland cement.¹⁸ These characteristics are important because C_3S typically makes up more than 50% of the material.¹⁸ Therefore, with a specific surface area of $50\text{ m}^2/\text{g}$, the setting time can be decreased by an even greater amount because it will hydrate faster, while providing the same strength to the cement.

A comparison was made between the low and high D.P. PVA, with reference to how the surface area changed with temperature increases. Figure 2 illustrates this behavior for C_2S as a representative case study for each of the components of Portland cement. It shows that as the calcination temperature increases, the specific surface area decreases. This occurred in the powders made by both the low and high D.P. PVA methods. The powder made with the low D.P. PVA exhibited a more negative slope than did the high D.P. PVA powder. This implies that the powder made by the low D.P. PVA method should have enhanced reactivity, finer particle size, and faster sintering.

Figure 3 shows the effect of the PVA content on the BET specific surface area. This experiment was conducted with C_4AF calcined at 700°C , with both the low D.P. and high D.P. PVA solutions. The data remained consistent with the results from Fig. 2, in

that the low D.P. PVA produced powders with higher surface areas. Furthermore, Fig. 3 illustrates that the more PVA used, the higher the surface areas in both the powders made from the low and high D.P. PVA. For systems in which not enough polymer is used, agglomeration may occur. One explanation for this may be that upon burnout, the agglomerated cation precursors lose most of the organics in the outer region. Due to the intense heat evolved from the oxidative process, polymer and organic components remain within the shell. Further application of heat causes the organics to decompose into gases and expand. The less-agglomerated particles have lost most or all of the organics with the application of heat. In the case of agglomeration, during the slow decomposition of organics, the agglomerated cations are oxidized. Thus, a large powder particle size distribution is observed. To maximize the powder properties, therefore a balance is needed between cations and the amount of polymer.

(3) *Powder Morphology*

Figures 4 and 5 illustrate the morphologies of crystalline powders calcined at the lowest crystallization temperature for each compound. In the powders prepared by the high D.P. PVA method (Fig. 4), particle necking resulting from sintering was observed except in the C_4AF powder which crystallized at low temperatures. The pre-sintering resulted from the exceedingly high specific surface area and hence enhanced reactivity of the C_3A and C_3S powders, which needed a relatively high crystallization temperature to completely react all the CaO . The C_4AF powder showed a particle size distribution in the range from 50 nm to 400 nm.

In general, the powders derived from the low D.P. PVA were more reactive than were the powders prepared from the high D.P. PVA. For example, in the case of C_3A , the microstructure was more dense with smaller individual particle sizes (Fig. 5(c)), in comparison with the C_3A derived from the high D.P. PVA (Fig. 4(c)), despite a lower crystallization temperature for the low D.P. PVA method. This suggests that the low D.P. PVA method is more effective in making fine and reactive powders than the high D.P. PVA method. C_3S prepared from the low D.P. PVA showed the same tendency as did the C_3A powder (Figs. 5(b) and 4(b)). The C_2S powder in the low D.P. PVA route was crystallized before the onset of sintering. It was possible to retain a small particle size (≈ 100 nm) without particle necking at its low crystallization temperature of $700^\circ C$ (Figs. 5(a) and 4(a)). Agglomerates of approximately $1.5\ \mu m$ in size were observed. C_4AF powder derived from the low D.P. PVA process exhibited nearly the same result as that obtained from the high D.P. PVA system (Figs. 5(d) and 4(d)).

The morphologies of the attrition-milled C_3S and C_3A powders are seen in Fig. 6. Before attrition-milling, C_3S and C_3A powders showed quite a dense morphology because of sintering. However, attrition-milling for 1 h was effective in breaking up the porous necked particles. This was clearly demonstrated for the C_3S and C_3A powders (Figs 4(b) and 6(a) and Figs. 5(c) and 6(b), respectively). In both cases, attrition-milling resulted in significant increases in specific surface area (Table IV) and hence reactivity.

IV. Conclusion

The four component powders of Portland cement have been synthesized by the PVA solution-polymerization route. The length of PVA polymer chain and its amount affected the homogeneity and distance between metal ions in the organic/inorganic precursor during the steric entrapment mechanism. More reactive powders having higher specific surface areas were obtained by a low degree of polymerization in the PVA method. A ratio of 4:1 cation valences to $(OH)^-$ functional groups produced optimum powder characteristics. The low crystallization temperature and high specific surface area of the chemically synthesized powders can economize the process of making Portland cement, enhance setting speed, increase strength, and lead to other desirable characteristics. The low specific surface area of the coarse, sintered powder could be improved to a higher specific surface area by an effective attrition-milling process.

V. Acknowledgments:

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Figure Captions

Figure 1: The volume fraction of C_3A powder synthesized as a function of the ratio of positively charged cations to negatively charged $(OH)^-$ groups in the PVA polymer.

Figure 2: The decrease in BET specific surface area for C_2S powders with increasing calcination temperature increases (1 h holding time).

Figure 3: The variation of BET specific surface areas for C_4AF as a function of the ratio of positively charged cations to negatively charged $(OH)^-$ groups in the PVA polymer.

Figure 4: The morphologies of crystalline powders for the four components of Portland cement made by the high degree of polymerization PVA process at optimum PVA content (Table II) (a) C_2S powder as-calcined at 900°C for 1 h, (b) C_3S powder as-calcine at 1400°C for 2 h, (c) C_3A powder as-calcined at 1100°C for 3 h and (d) C_4AF powder as-calcined at 700°C for 1 h.

Figure 5: The morphologies of crystalline powders for the four components of Portland cement made by the low degree of polymerization PVA process at optimum PVA content (Table III) (a) C_2S powder as-calcined at 800°C for 1 h, (b) C_3S powder as-calcine at 1400°C for 1 h, (c) C_3A powder as-calcined at 1000°C for 1 h and (d) C_4AF powder as-calcined at 700°C for 1 h.

Figure 6: The micrographs of 1 h attrition-milled crystalline powders for (a) C_3S prepared by the high D.P. PVA method and (b) C_3A made by the low D.P. PVA method. See also Table IV.

Table I. Powder Preparation and Processing Variables

	Chemical agents	pH adjustment	Solution color	Burnout temp.(°C)	Properties of organic/inorganic precursor
C ₂ S	Calcium-nitrate [‡] + Ludox SK	Nitric acid adj pH: 2	Transparent	3°C/min, 1hr hold at 700°C	White precursor fairly coarse texture hydrophilic
C ₃ S	Calcium nitrate + Ludox SK	Nitric acid adj pH: 2	Transparent	3°C/min, 1hr hold at 700°C	White precursor coarse texture hydrophilic
C ₃ A	Calcium nitrate + Aluminum nitrate [†]		Transparent	3°C/min 1hr hold at 700°C	Yellow precursor soft and porous texture hydrophilic
C ₄ AF	Calcium nitrate + Aluminum nitrate + Iron nitrate [§]		Transparent	3°C/min 1hr hold at 700°C	Red/brown precursor soft and porous texture hydrophilic

[‡] Ca(NO₃)₂•4H₂O (reagent grade, Aldrich Chem. Co., Milwaukee, WI)

[†] Al(NO₃)₃•9H₂O (reagent grade, Aldrich Chem. Co., Milwaukee, WI)

[§] Fe(NO₃)₃•9H₂O (reagent grade, ALFA Aesor Chem. Co., Ward Hill, MA)

Table II. Crystallization Behavior from High Degree of Polymerization PVA

Temperature (°C)	C ₂ S (4:1)	C ₃ S (8:1)	C ₃ A (8:1)	C ₄ AF (8:1)
600	amorphous	amorphous	amorphous	amorphous
700	amorphous+ α'_L -Ca ₂ SiO ₄	amorphous	Ca ₃ Al ₂ O ₆ < CaO	Ca ₄ Al ₂ Fe ₃ O ₁₀
800	α'_L -Ca ₂ SiO ₄ +CaO < β -Ca ₂ SiO ₄	β -Ca ₂ SiO ₄ +CaO+Ca ₃ SiO ₅	Ca ₃ Al ₂ O ₆ < CaO	Ca ₄ Al ₂ Fe ₃ O ₁₀
900	α'_L -Ca ₂ SiO ₄ + [CaO] < β -Ca ₂ SiO ₄	β -Ca ₂ SiO ₄ +CaO+Ca ₃ SiO ₅	Ca ₃ Al ₂ O ₆ > CaO	Ca ₄ Al ₂ Fe ₃ O ₁₀
1000	β -Ca ₂ SiO ₄ + [CaO]	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆ > CaO	Ca ₄ Al ₂ Fe ₃ O ₁₀
1100	β -Ca ₂ SiO ₄ + [CaO]	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆ + [CaO]	Ca ₄ Al ₂ Fe ₃ O ₁₀
1200	β -Ca ₂ SiO ₄	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆ + [CaO]	Ca ₄ Al ₂ Fe ₃ O ₁₀
1300	γ -Ca ₂ SiO ₄ [*]	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆	Ca ₄ Al ₂ Fe ₃ O ₁₀
1400	γ -Ca ₂ SiO ₄	Ca ₃ SiO ₅ + [CaO]	Ca ₃ Al ₂ O ₆	Ca ₄ Al ₂ Fe ₃ O ₁₀

() : Optimum PVA content in terms of ratio of cation valences to (OH)⁻ functional groups, for lowest crystallization temperature.
[] : much smaller amounts relative to other phases present.

Table III. Crystallization Behavior from Low Degree of Polymerization PVA

Temperature (°C)	C ₂ S (4:1)	C ₃ S (4:1)	C ₃ A (4:1)	C ₄ AF (4:1)
600	amorphous + α'L-Ca ₂ SiO ₄	amorphous	amorphous	amorphous
700	α'L-Ca ₂ SiO ₄ +CaO <β- Ca ₂ SiO ₄	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆ < CaO	Ca ₄ Al ₂ Fe ₃ O ₁₀
800	α'L-Ca ₂ SiO ₄ + [CaO] <β- Ca ₂ SiO ₄	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆ > CaO	Ca ₄ Al ₂ Fe ₃ O ₁₀
900	β- Ca ₂ SiO ₄ + [CaO]	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆ > CaO	Ca ₄ Al ₂ Fe ₃ O ₁₀
1000	β- Ca ₂ SiO ₄ + [CaO]	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆ + [CaO]	Ca ₄ Al ₂ Fe ₃ O ₁₀
1100	β- Ca ₂ SiO ₄	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆ + [CaO]	Ca ₄ Al ₂ Fe ₃ O ₁₀
1200	γ- Ca ₂ SiO ₄	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆	Ca ₄ Al ₂ Fe ₃ O ₁₀
1300	γ- Ca ₂ SiO ₄	Ca ₃ SiO ₅ +CaO	Ca ₃ Al ₂ O ₆	Ca ₄ Al ₂ Fe ₃ O ₁₀
1400	γ- Ca ₂ SiO ₄	Ca ₃ SiO ₅ + [CaO]	Ca ₃ Al ₂ O ₆	Ca ₄ Al ₂ Fe ₃ O ₁₀

() : Optimum PVA content in terms of ratio of cation valences to (OH)⁻ functional groups, for lowest crystallization temperature.
 [] : much smaller amounts relative to other phases present.

Table IV. BET Specific Surface Area of Each Crystallized Compound at Optimum PVA Content

Powder	C ₂ S	C ₃ S	C ₃ A	C ₄ AF
High degree of polymerization PVA	Crystallization temp. (°C)	900	1400	1100
	Holding time (h)	1	2	3
	BET S.S.A. (m ² /g)	12.9	0.9	2.3
Low degree of polymerization PVA	Crystallization temp. (°C)	800	1400	1000
	Holding time (h)	1	1	1
	BET S.S.A. (m ² /g)	22.1	0.8	4.2
	BET S.S.A. (m ² /g) (after attrition milling for 1 h)		50 [§]	18.9 [†]

[§] High DP PVA method

[†] Low DP PVA method

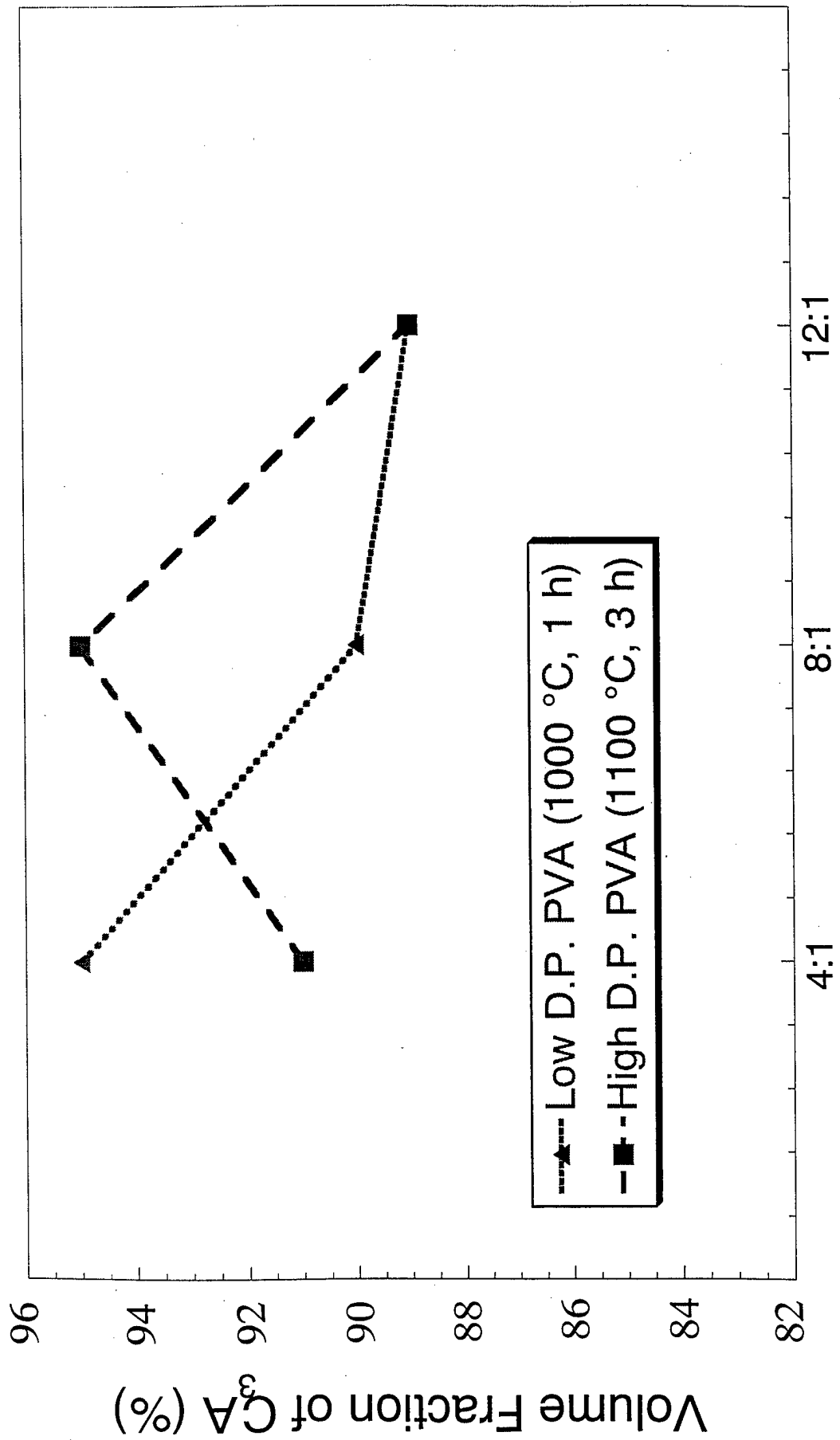
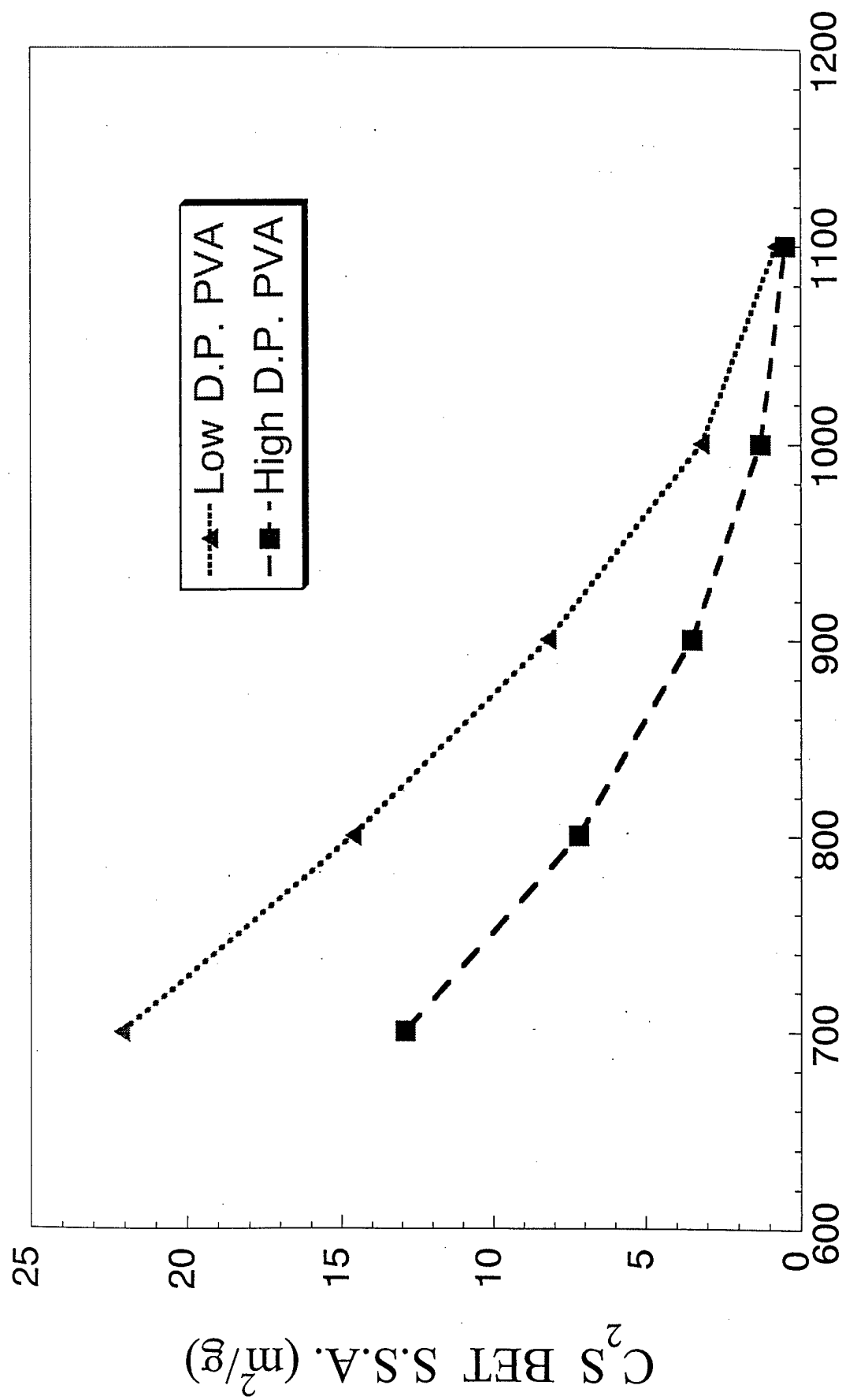


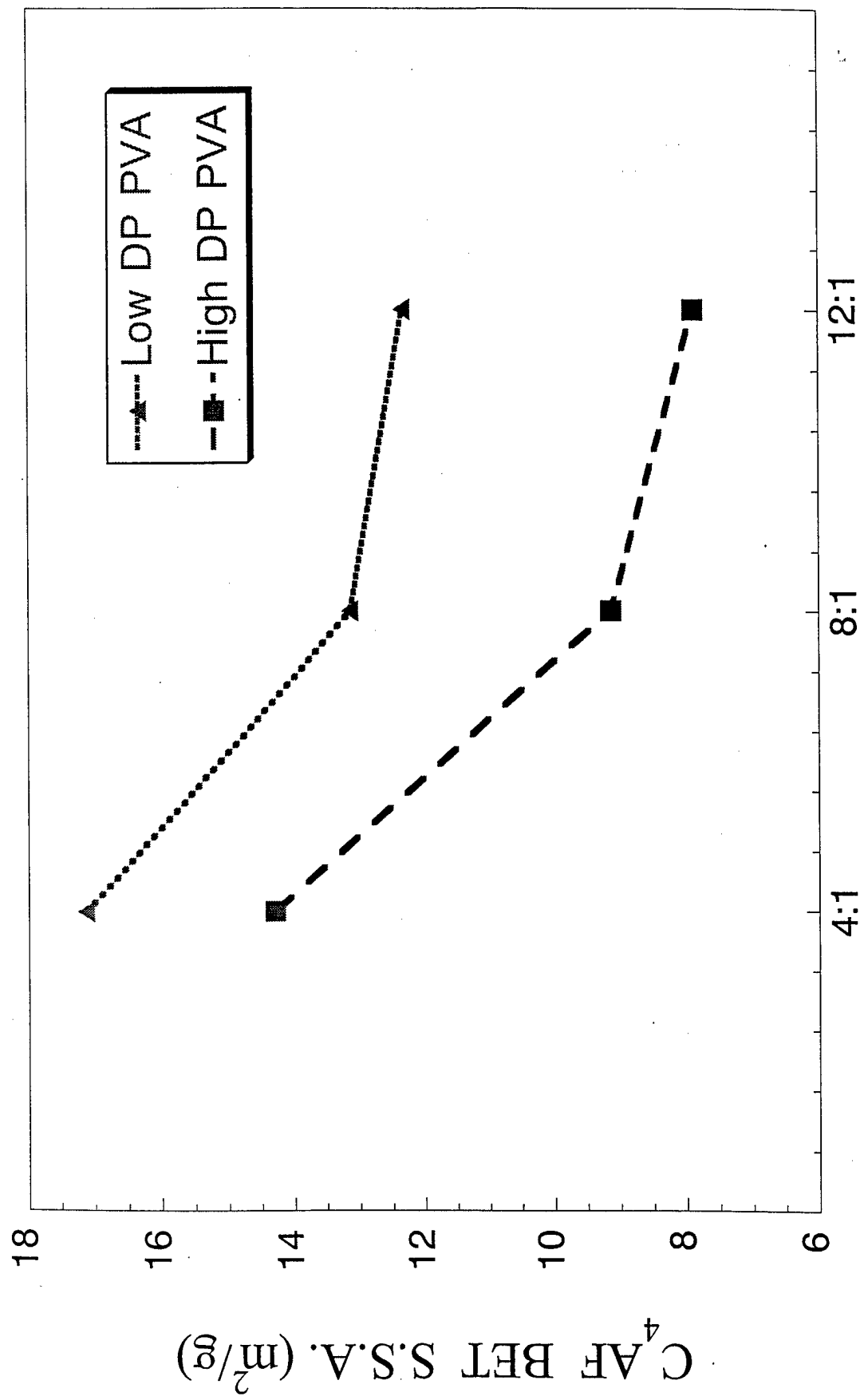
Fig. 1



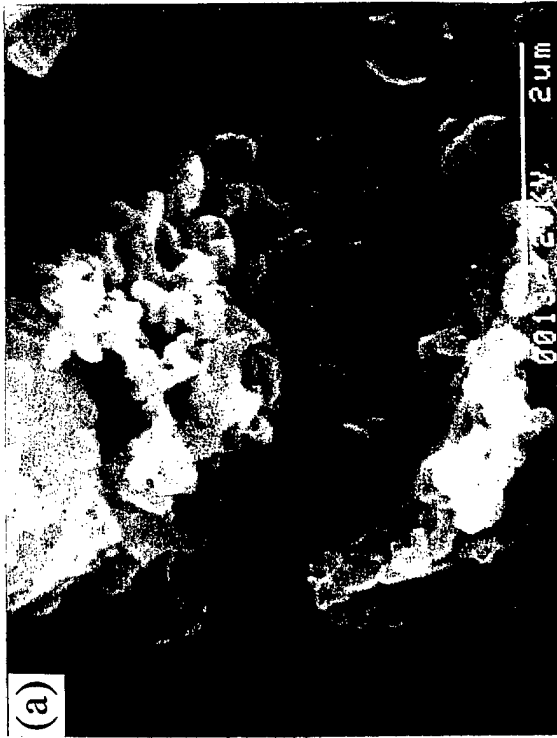
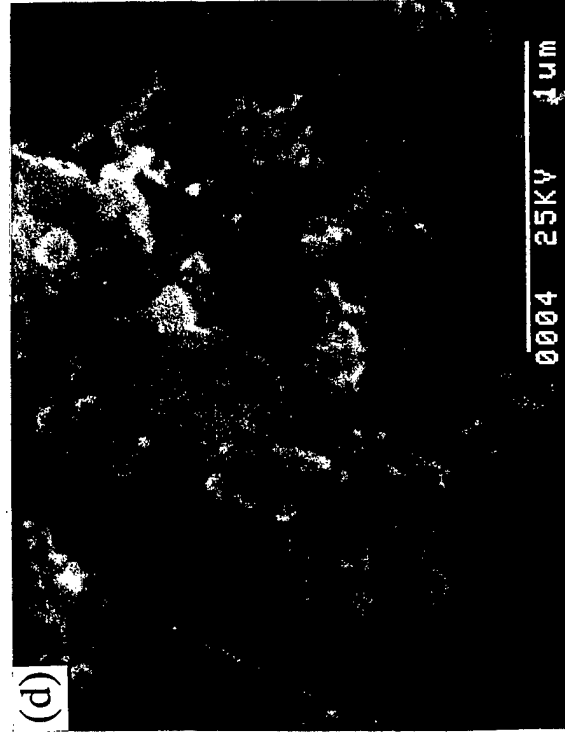
Calcination Temperature (°C) for 1 h

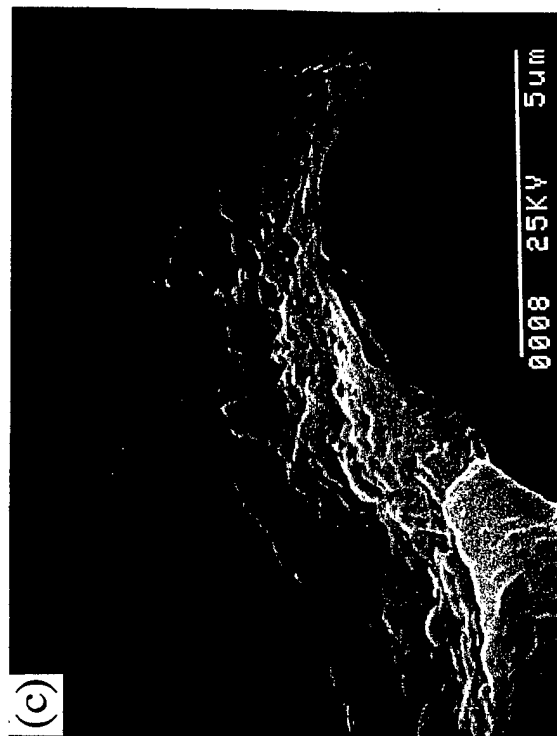
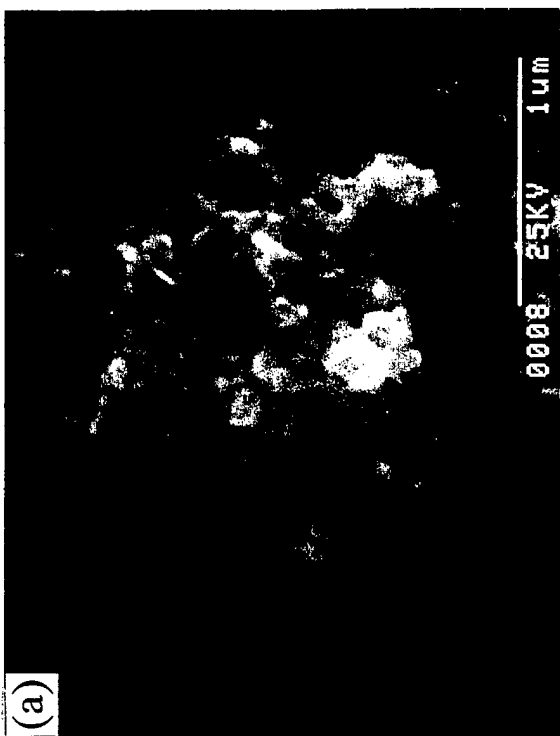
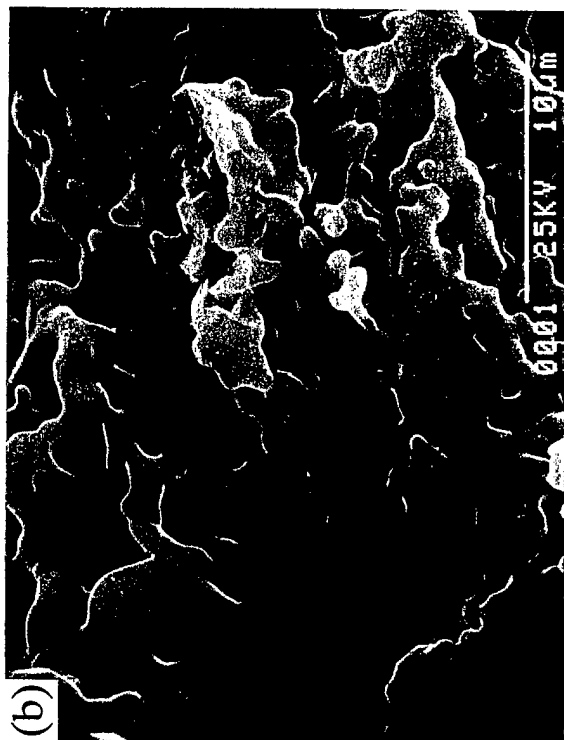
Fig. 2

Fig. 2



Ratio of cation to $(OH)^-$ groups in the PVA
 (≤----increasing PVA content)





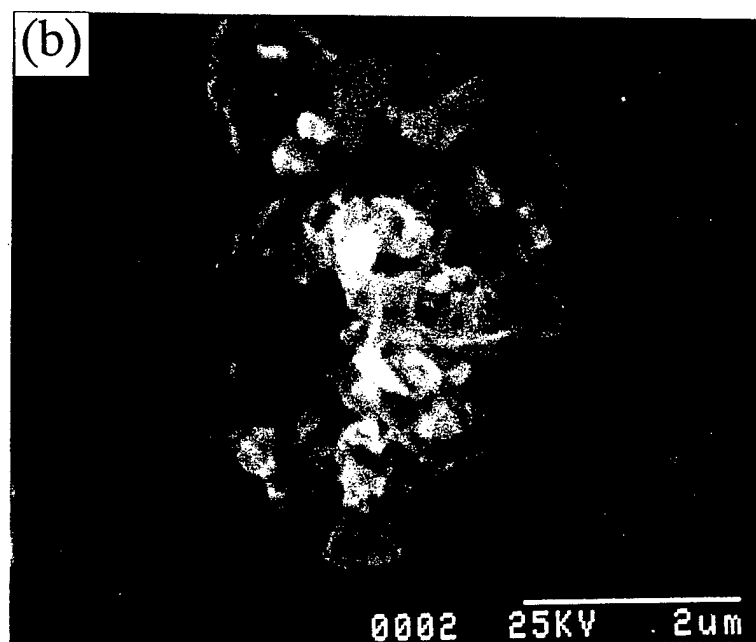
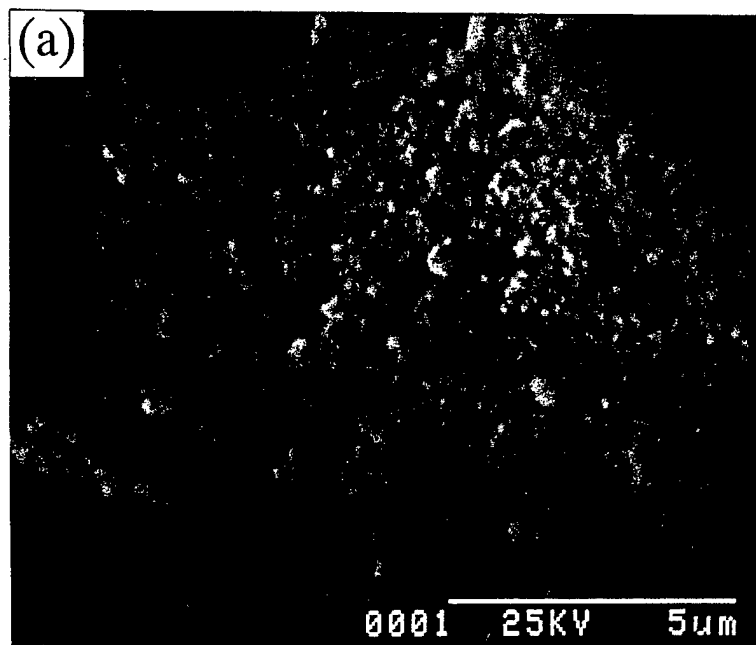


Fig. 6